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71 Applicant: **AUSIMONT S.p.A.**
31, Foro Buonaparte
I-20121 Milano(IT)

72 Inventor: **Braga, Vittorio**
12, Via G. Meli
I-44100 Ferrara(IT)
Inventor: **Ghisellini, Renato**
134, Viale Cavour
I-44028 Poggio Renatico, Ferrara(IT)

74 Representative: **Weinhold, Peter, Dr. et al**
Patentanwälte Dipl.-Ing. G. Dannenberg Dr.
P. Weinhold Dr. D. Gudel Dipl.-Ing. S.
Schubert Dr. P. Barz Siegfriedstrasse 8
W-8000 München 40(DE)

54 **Crosslinked polypropylene compositions suitable for the manufacture of foamed articles.**

57 Described are polypropylene compositions which are particularly suitable for the preparation of foamed articles and which comprise a mixture of

a) 3 to 75% by weight of crosslinked polypropylene

b) 97 to 25% by weight of not crosslinked polypropylene having an intrinsic viscosity of from 0.5 to 1.3 dl/g; which is characterized by a M.I. (230 °C, 2.16 kg) of from 0.001 to 600 kg/10' and a dispersion of the crosslinked polypropylene in the not crosslinked polypropylene in the form of gels.

Also disclosed is a process for the preparation of the above compositions.

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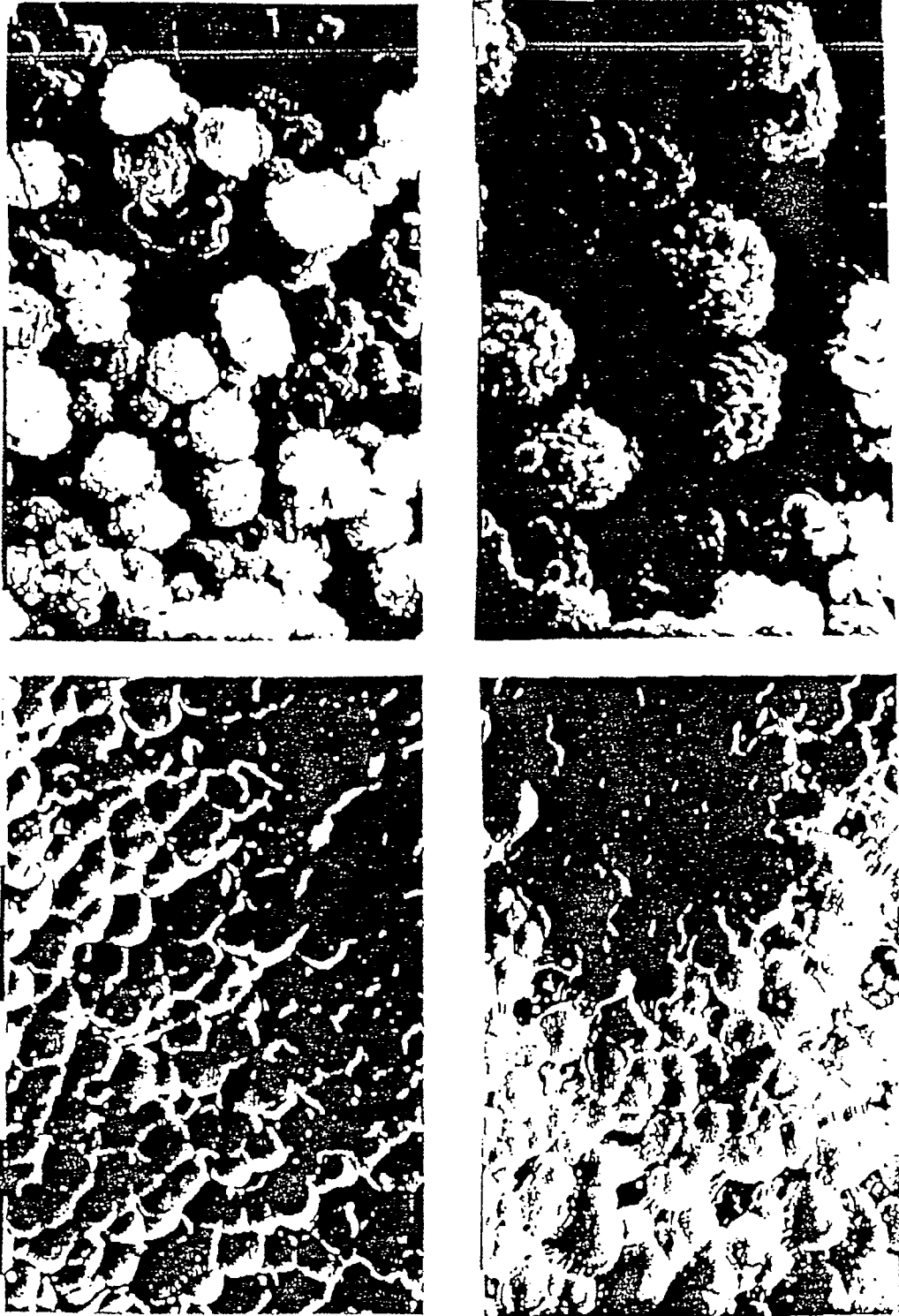


FIG. 1

The present invention relates to compositions consisting of or comprising an intimate mixture of crosslinked polypropylene and of not crosslinked polypropylene, suitable for the manufacture of foamed articles.

5 Compositions and manufactured articles comprising crosslinked polypropylene and not crosslinked polypropylene, obtained by the crosslinking of polypropylene with organic peroxides and crosslinking co-
agents having double or triple bonds, optionally in the presence of foaming agents, are known from EP-A-73435.

10 According to said document the preformed manufactured article to be crosslinked is treated, at the crosslinking temperature, in an autoclave containing an aqueous solution of the peroxide and of the co-agent. Alternatively, the manufactured article, obtained by the extrusion, at 160 to 180 °C, of a mixture comprising polypropylene, the peroxide and the co-agent, is separately crosslinked at 180 to 230 °C and atmospheric, reduced or superatmospheric pressure.

These compositions show a poor homogeneity and can be processed only with difficulty. Moreover, the foamed articles obtained therefrom do not have the flexibility required for many applications.

15 There have now been found polypropylene compositions which are endowed with highly satisfactory processing characteristics and a high homogeneity which makes them suitable for the manufacture of foamed materials having extraordinarily small and regular cells. These compositions, which are one of the objects of the present invention, comprise an intimate blend of from 3 to 75% by weight of crosslinked polypropylene and from 97 to 25% by weight of not crosslinked polypropylene, wherein:

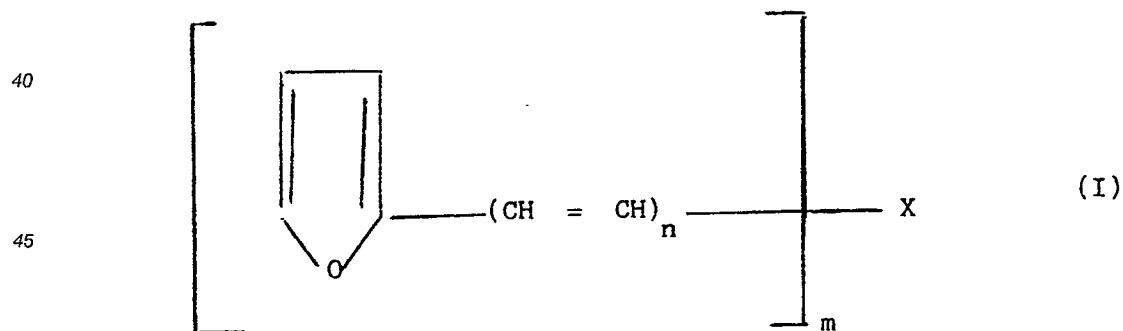
- 20 a) the intrinsic viscosity (η) at 135 °C in tetrahydronaphthalene of the not crosslinked polypropylene ranges from 0.5 to 1.3 dl/g, preferably from 0.6 to 1.3 and most preferably from 0.9 to 1.0 dl/g;
b) the melt index (at 230 °C and 2.16 kg) ranges from 600 to 0.001 kg/10', preferably from 80 to 0.01 kg/10';
c) the crosslinked polypropylene is present as dispersed phase in the not crosslinked polypropylene (matrix) in the form of gels showing approximately spheric particles having sizes of from 0.5 to 100 μ m, preferably 0.5 to 10 μ m and more preferably 0.5 to 5 μ m.

The term "crosslinked polypropylene" is meant to denote polypropylene which is insoluble in xylene at 135 °C. Accordingly the term "not crosslinked polypropylene" means polypropylene soluble in xylene at the above temperature.

30 Preferably, the above compositions comprise from 7 to 40% by weight of crosslinked polypropylene and from 93 to 60% by weight of not crosslinked polypropylene.

The compositions of the present invention may be obtained by subjecting a mixture comprising:

- 35 a) isotactic polypropylene,
b) a crosslinking agent for the polypropylene of the peroxidic type;
c) from 5 to 500%, preferably from 7 to 150% by weight, calculated on the peroxidic agent, of a compound (co-agent) of one of the following general formulae:



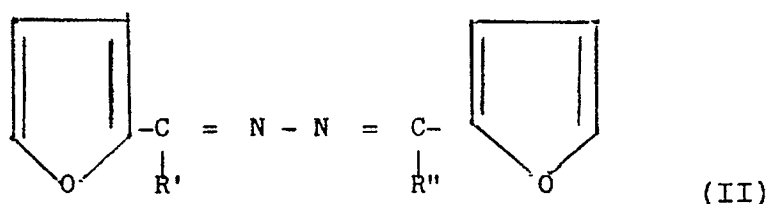
50 wherein X is selected from CHO, COOH, CONH₂, CN, NO₂, -COOCO-, COOR, -CO-, CH₂COCH₂COOR and -CH(COOR)₂ radicals wherein R is a C₆-C₈ aryl (e.g. phenyl), or a C₁-C₄ alkyl (e.g. methyl or ethyl) group;

n = 1 or 2; and

m = an integer corresponding to the free valence of X;

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10 wherein R' and R'', the same or different from each other, are selected from hydrogen, C₁-C₄ alkyl radicals (e.g. CH₃ and C₂H₅) and C₅-C₈, preferably C₆-C₈ cycloalkyl groups, to mastication or to the action of other shear forces, at a temperature sufficient to melt the polypropylene and at which the crosslinking of the polypropylene can occur.

15 Preferred examples of furane derivatives of formulae (I) and (II) which can be used in the present invention are 1,5-difurfuryl-1,4-pentadiene-3-one and difurfuraldazine.

Other suitable examples are, e.g., the furane compounds described in US-A-3,301,837, some examples of which are: β-(alpha-furyl)acrolein; 5-(alpha-furyl)-pentadienal; β-(alpha-furyl)-acrylamide; β-(alpha-furyl)-acrylonitrile; β-(alpha-furyl)acrylic acid and esters thereof; bis-furfurylideneacetone; β-(alpha-furyl)ethyl-β-(alpha)acrolein; esters of furfurylidene malonic acid; condensation products of β-(alpha-furyl)acrolein with
20 cyclic ketones, as described in Chem. Berichte 76, 676 (1943).

The above compounds are known in the art and can be prepared, e.g., according to the process of US-A-3,301,827.

The polypropylene may be a homopolymer or a copolymer of propylene with other copolymerizable olefinic monomers such as, for instance, ethylene, butene-1, butadiene, preferably in quantities up to 10%
25 by weight and generally in amounts of from 0.5 to 10% by weight of the copolymer. The corresponding copolymers may be either of the block type (heterophasic) or of the random type.

The peroxidic crosslinking agent is an organic peroxide, preferably selected from those showing a half-life of the order of from about 10 to about 400 seconds at the crosslinking temperatures. This temperature preferably ranges from about 150 to about 240 °C.

30 Examples of peroxides which can be used are: dicumylperoxide; alpha, alpha'-bis-(t.butylperoxy)-m-, and/or p-diisopropylbenzene (TBPDB); 1,1-di(t.butylperoxy)-3,5,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di-(t.butylperoxy)hexane.

The employed amounts of the crosslinking agent and of the co-agent depend on the desired percentage of crosslinked polypropylene in the final composition. These quantities may easily be calculated according to criteria well known to those skilled in the art, based on the activity and functionality of both the
35 crosslinking agent and the co-agent used. For the purposes of the present invention, said amounts will generally range from 0.1 to 5% by weight of the polypropylene weight.

The process for the preparation of the compositions of the present invention generally comprises the preparation of an intimate mixture of the above components (a) to (c) and the subsequent heating thereof
40 during the mixing or the mastication step or under the action of other shear forces, at a temperature which is at least equal to the melting temperature of the polypropylene and at which the crosslinking of polypropylene can take place.

The duration or the end of the crosslinking under these conditions is dependent on the quantity of the crosslinking agent used, calculated in a manner such as to obtain a composition containing from 3 to 75%
45 by weight of crosslinked polypropylene, based on the total polypropylene.

Generally, the crosslinking temperature is kept, as mentioned above, at from about 150 to about 240 °C, preferably from about 180 to about 240 °C.

The crosslinking is complete when the crosslinking agent is no longer present in the composition.

50 Mineral fillers, organic and/or inorganic pigments, stabilizers and additives which are generally used in olefinic and non-olefinic polymers, as well as quantities of up to 10% by weight of EPM rubbers can also be present in the preparation of the compositions of the present invention, together with components (a) to (c).

The preparation of the starting mix of components (a) to (c) and the optional additives, as well as the crosslinking of the mix itself may be performed in suitable apparatus such as, for instance, a Banbury mixer or a screw extruder of the Buss type or of the double-screw type, provided with mixing elements.

55 Preferred devices are those having creep gradients of from 350 to 5000 s⁻¹, preferably 500 to 3000 s⁻¹.

The particular morphology of the compositions of the present invention (Fig. 1) characterizes the type of crosslinking and differentiates these compositions from those which are obtained by crosslinking under static conditions. In fact, in the latter case the morphology of the compositions is geometrically less defined,

and in general it is of the interpenetrating type (see Fig. 2) with a behaviour under heating similar to that of a crosslinked elastomer. That is also the reason why these compositions as such are so poorly processable.

The compositions of this invention are characterized by a high melt strength and an elastomeric behaviour of the melt itself in connection with low creep gradients, although they remain surprisingly
5 processable.

The compositions of the present invention are particularly suitable for use in the manufacture of foamed materials.

For this purpose it is possible to work by incorporating a foaming agent into the crosslinked product, then extruding the mixture using a homogenizing single-screw extruder which shows and maintains up to
10 the head a reduction decrease of clearance between throat and chambers, thereby allowing the expansion to occur at the outlet.

Alternatively, it is possible to work in an injection press having a profile of the homogenizing screw which keeps the mixture of the polypropylene composition and the foaming agent under pressure and using a mould provided with air breathers. In both cases the extruder temperature preferably ranges from about
15 180 to about 200 °C.

According to another method, the foamed material can be obtained during the preparation of the crosslinked composition, by feeding into a double-screw extruder a mixture of not crosslinked polypropylene and co-agent, while introducing into the molten material both the crosslinking agent and the foaming agent at a distance from said feeding point equal to 2/3 of the extruder length and allowing the
20 whole mixture to proceed along the extruder under conditions of reduced volume up to the outlet.

In this case, the temperature is generally kept at from about 170 to about 200 °C.

The employable foaming agents can be of both chemical and physical type. In the first case their decomposition temperature should range from about 170 to about 220 °C.

Examples of foaming agents of the chemical type which may be used are azodicarbonamides, sulfonylhydrazides, dinitropentamethylenetetramine, p-toluenesulfonylsemicarbazide, trihydrazine-triazine
25 and generally all products used in the art for said purpose, having decomposition temperatures at least equal to the melting temperature of polypropylene.

As physical foaming agents all those known in the literature for said purpose can be used, for instance chlorofluorocarbons and aliphatic hydrocarbons containing a low number of carbon atoms (such as, for
30 instance, propane, butane, pentane etc.).

The foamed materials thus obtained (and which are a further object of the present invention) comprise a mixture of from 3 to 75% by weight of crosslinked (preferably isotactic) polypropylene and of from 97 to 25% by weight of not crosslinked polypropylene having an intrinsic viscosity of from 0.5 to 1.3 dl/g, said mixture showing a MI of from 600 to 0.001 kg/10' (measured at 230 °C and 2.16 kg). Said foamed materials
35 are of the closed cell type and usually have a density of from 0.2 to 0.4 g/cm³.

EXAMPLES 1 - 13

These examples illustrate the preparation of the compositions according to the invention, using
40 crosslinking agents, co-agents and different polymers. Working conditions and characteristics of the obtained compositions are listed in Table 1.

The compositions were prepared by allowing the polypropylene to melt by heating it at 180 °C in an inner mixer of the Brabender type (60 rpm) and then adding the co-agent and thereafter the crosslinking agent.

45 The compositions were continuously mixed at the above temperature for about 10 minutes, under a creep gradient of about 350 to 700 sec⁻¹.

After this period of time, active peroxide was no longer present in the compositions.

EXAMPLES 14 AND 15

50 These examples illustrate the preparation of compositions according to the invention by extrusion.

To this end a double-screw extruder of the MARRIS type (L/D = 30, diameter = 33 mm) was employed, working at 150 rpm and at a temperature of from 180 to 230 °C.

A mixture of polypropylene and crosslinking co-agent (obtained in a dry mixer) was introduced into the
55 extruder, while adding the crosslinking agent at a distance from the introduction zone equal to 2/3 of the extruder length.

The creep gradient under which the mixture was extruded was about 2000 sec⁻¹ in example 15 and about 3000 sec⁻¹ in example 14.

The thus obtained product was then molded in an injection press (Negri and Bossi N60) working at 200 °C, with the mold being kept at 40 °C and under an injection pressure of 30%.

The crosslinking working conditions and the characteristics of the samples thus prepared are reported in Table 2.

5 Crosslinked compositions obtained as described above were further used for the preparation of foamed materials, either by extrusion or by press-injection according to the following modalities.

Extrusion

10 The operation was carried out with a single screw Brabender extruder (L/D = 20, diameter = 20 mm, diameter of the head matrix = 2 mm) working at a temperature of 180 to 200 °C along the body and of 150 to 190 °C at the head, introducing a mixture prepared in a dry mixer and consisting of compositions of the above examples, crosslinked with 0.5% by weight of azodicarbonamide.

15 Press-injection

The operation was carried out with a Negri and Bossi N60 press (temperature of the cylinder: 200 °C; temperature of the mold equipped with breather channels: 40 to 50 °C; injection pressure: 30 to 90%), using the same mixture with azodicarbonamide already used for the preparation by extrusion.

20 The characteristics of the foamed materials are reported in Table 2.

EXAMPLE 16

25 This example relates to the manufacture of foamed materials according to the invention, concurrently with the preparation of the crosslinked composition.

To this end, a mixture of polypropylene (M.I. = 8) and difurfuralaldazine was fed into a double-screw extruder working at a temperature of 180 to 200 °C along the body and of 150 to 190 °C at the head under a creep gradient of about 2800 sec⁻¹, while introducing in the extruder, at a distance from said feeding point equal to 2/3 of the extruder length, the peroxide and the foaming agent (azodicarbonamide).

30 Table 3 lists the amounts of reactants and the characteristics of the foamed product.

T A B L E 3

35	Polypropylene	parts by weight	100
	Difurfuralaldazine	"	0.45
40	Peroxide (TBPDB)	"	3
	Azodicarbonamide		0.5
	<u>Characteristics of the</u>		
45	<u>obtained product</u>		
	Density	g/cm ³	0.25
	Homogeneity	-	very good

50

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TABLE 1

Compa- rison	1	2	3	4	5	6	7	8	9	10	11	12	13		
		100	100	100	100	100	100	-	-	-	-	-	-	-	
Polypropylene (M.I.=0.7)*	parts by weight	-	-	-	-	-	-	-	-	-	-	-	-		
Polypropylene (M.I.=8) *	parts by weight	-	-	-	-	100	-	-	-	-	-	-	100		
Polypropylene (M.I.=25)	parts by weight	-	-	-	-	-	-	100	-	-	-	-	-		
Statistic copolymer of polypropylene with															
2% of ethylene (M.I.=8)	parts by weight	-	-	-	-	-	-	-	100	-	-	-	-		
Block copolymer of polypropylene with															
2% of ethylene (M.I.=3.5) **	parts by weight	-	-	-	-	-	-	-	-	100	-	-	-		
Polypropylene (M.I.=8)+10% EPH	parts by weight	-	-	-	-	-	-	-	-	-	100	100	-		
Di-furfural-aldazine (coag)	parts by weight	0.22	0.45	0.9	0.76	1.5	1.3	0.76	0.76	0.76	0.45	0.76	-		
Peroxide (TBPDB)	parts by weight	3	3	3	5	5	9	5	5	5	3	5	3		
1,5-difurfuryl-															
1,4-pentadiene-3-one	parts by weight	-	-	-	-	-	-	-	-	-	-	-	0.45		
Characteristics of the composition															
after cross-linking															
Gross-linked polypropylene	%	3.0	7.6	12	39	40	63	71	23	35	43	34	10	41	17
Intrinsic viscosity of the															
not cross-linked polypropylene	dl/g	<0.4	0.75	0.90	0.88	0.58	0.55	0.50	0.62	0.60	0.64	0.70	1.25	1	0.91
M.I. (230°C, 2.16 kg)	kg/10'	>700	610	1.40	-	0.18	-	-	0.36	0.20	0.045	0.095	5.71	0.28	1.95
M.I. (230°C, 5.00kg)	kg/10'	-	-	-	0.94	-	-	-	-	-	-	-	-	-	-
M.I. (230°C, 10.00 kg)	kg/10'	-	-	-	-	-	1.09	0.85	-	-	-	-	-	-	-
Gel size															
All the particles had size between 0.5 and 100 μ, with 60% thereof having size between 5 and 40 μ.															

* Measured at 230°C; 2.16 kg

** Containing 72% by weight of ethylene, and having Mooney viscosity (1+4)100°C = 28

T A B L E 2

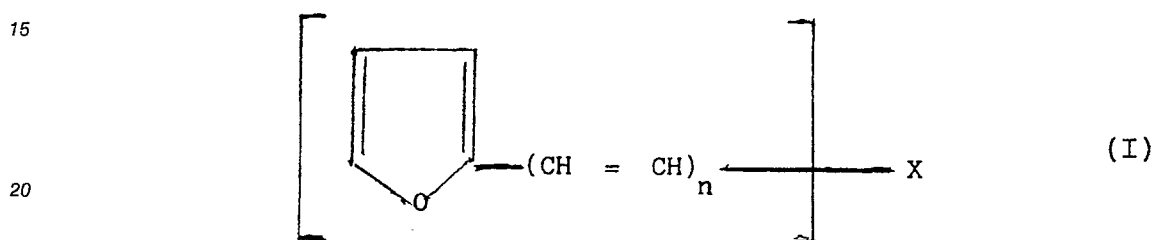
		<u>E X A M P L E S</u>		
		14	15	
5	Polypropylene (M.I.=8)	parts by weight	100	-
	Statistic copolymer of propylene with 10% of ethylene (M.I.=8)	parts by weight	-	100
10	Difurfural aldazine	parts by weight	0.45	0.76
	Peroxide (TBPDB)	parts by weight	3	5
<u>CHARACTERISTICS OF THE COMPOSITION AFTER CROSS-LINKING</u>				
15	Cross-linked polypropylene	%	3	25
	M.I. (230°C; 2.16 kg)		39	5
<u>CHARACTERISTICS OF THE MOLDED SAMPLES</u>				
	Rockwell hardness		101	87
	Ultimate tensile strength	MPa	21.5	19.2
20	Ultimate elongation	%	3	5
	Flexural modulus at 23°C	MPa	1420	940
	Izod (notch) at 23°C	J/m	13	23
	Vicat (1 kg)	°C	142	125
25	HDT* at 0.46 MPa	°C	112	85
<u>CHARACTERISTICS OF FOAMED MATERIALS</u>				
<u>By extrusion</u>				
	. density	g/cm ³	0.3	0.2
	. homogeneity		very good	very good
30	<u>By press -injection</u>			
	. density	g/cm ³	0.3	0.2
	. homogeneity		very good	very good
35	* heat deflection temperature			

Claims

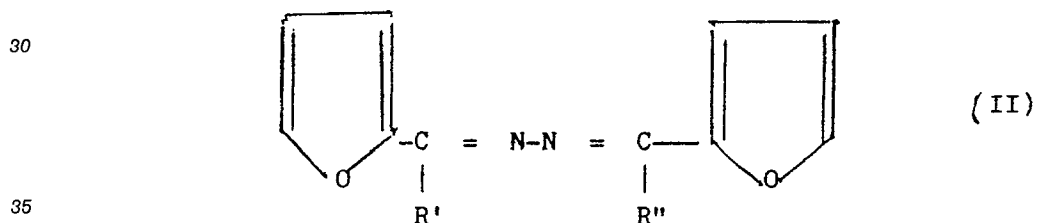
- 40 1. Compositions comprising a mixture of:
 - (a) from 3 to 75% by weight of crosslinked polypropylene
 - (b) from 97 to 25% by weight of not crosslinked polypropylene having an intrinsic viscosity in tetrahydronaphthalene at 135 °C of from 0.5 to 1.3 dl/g.
- 45 said mixture having a melt index (M.I.), measured at 230 °C and 2.16 kg. of from 0.001 to 600 kg/10', the crosslinked polypropylene being dispersed in the not crosslinked polypropylene and being present therein in the form of a gel having a particle size of from 0.5 to 100 μm.
- 50 2. Compositions according to claim 1 wherein the not crosslinked polypropylene has an intrinsic viscosity in tetrahydronaphthalene at 135 °C of from 0.9 to 1.3 dl/g.
3. Compositions according to any one of claims 1 and 2, wherein the crosslinked polypropylene is present in the form of a gel having a particle size of from 0.5 to 10, and particularly 0.5 to 5 μm.
- 55 4. Compositions according to any one of claims 1 to 3, wherein the mixture has a M.I. at 230 °C and 2.16 kg of from 0.01 to 80 kg/10'.
5. Compositions according to any one of claims 1 to 4, wherein the crosslinked polypropylene in the

mixture accounts for 7 to 40% by weight and the not crosslinked polypropylene accounts for 93 to 60% by weight.

6. Compositions according to any one of claims 1 to 5, wherein the polypropylene is a copolymer containing up to 10% by weight of olefin different from propylene.
7. Process for the preparation of compositions according to any one of claims 1 to 6, wherein a mixture comprising:
- preferably isotactic polypropylene
 - a peroxidic crosslinking agent for the polypropylene and
 - from 5 to 500% by weight, based on the peroxidic crosslinking agent, of a compound of one of the general formulae (I) and (II):



wherein X is selected from CHO, COOH, CN, CONH₂, NO₂, -COOCO-, COOR, -CO-, CH₂COCH₂COOR and CH(COOR)₂ radicals wherein R is C₆-C₈ aryl or C₁-C₄ alkyl; n = 1 or 2; and m = an integer corresponding to the free valence of X;



wherein R' and R'', the same or different from each other, are selected from hydrogen, C₁-C₄ alkyl and C₅-C₈, preferably C₆-C₈ cycloalkyl groups; is subjected to crosslinking under shear at a temperature sufficient to melt the polypropylene and at which the crosslinking of polypropylene occurs, preferably in the presence of a foaming agent.

8. Process according to claim 7, wherein the mixture is crosslinked under a creep gradient of from 350 to 5000 sec⁻¹, particularly 500 to 3000 sec⁻¹.
9. Process according to any one of claims 7 and 8, wherein the compound of general formula (I) or (II) is present in an amount of from 7 to 150% by weight, based on the peroxidic crosslinking agent.
10. Process according to any one of claims 7 to 9, wherein the polypropylene is a copolymer containing up to 10% by weight of olefin different from propylene.
11. Process according to any one of claims 7 to 10, wherein the mixture contains up to 10% by weight of an ethylene/ propylene rubber.
12. Foamed materials, having a density of from 0.2 to 0.4 g/cm³ and comprising a mixture of:
- 3 to 75% by weight of crosslinked polypropylene
 - 97 to 25% by weight of not crosslinked polypropylene having an intrinsic viscosity in tetrahydronaphthalene at 135 °C of from 0.5 to 1.3 dl/g;

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said mixture having a M.I. (at 230 ° C, 2.16 kg) of from 0.001 to 600 kg/10'.

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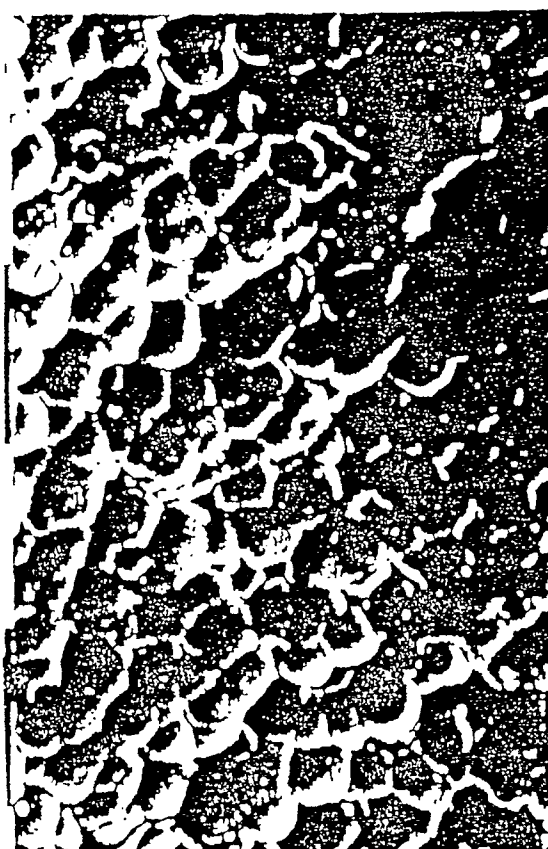
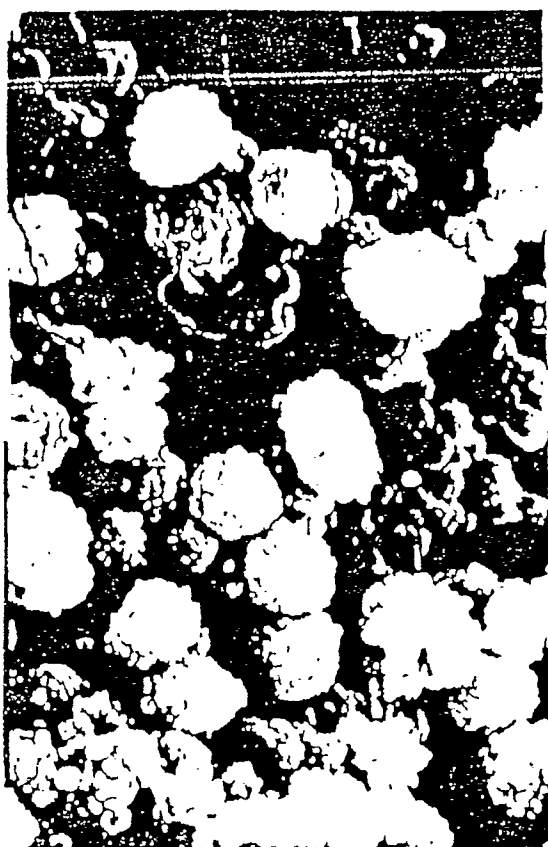


FIG. 1

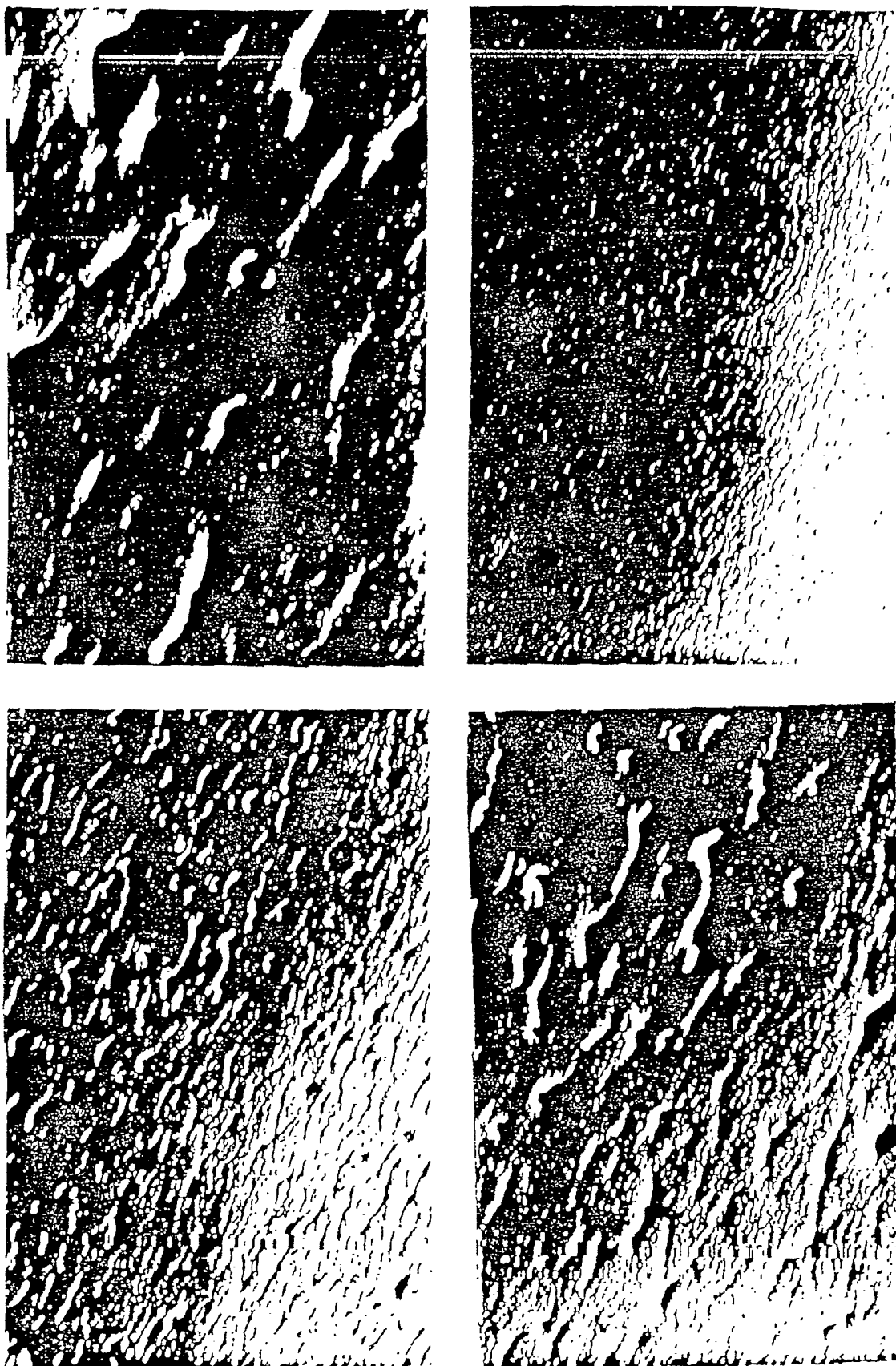


FIG. 2